

APPENDIX J

Partition Coefficients For Uranium

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J.1.0 Background

The review of uranium K_d values obtained for a number of soils, crushed rock material, and single-mineral phases (Table J.5) indicated that pH and dissolved carbonate concentrations are the 2 most important factors influencing the adsorption behavior of U(VI). These factors and their effects on uranium adsorption on soils are discussed below. The solution pH was also used as the basis for generating a look-up table of the range of estimated minimum and maximum K_d values for uranium.

Several of the studies identified in this review demonstrate the importance dissolved carbonate through the formation of strong anionic carbonate complexes on the adsorption and solubility of dissolved U(VI). This complexation especially affects the adsorption behavior of U(VI) at alkaline pH conditions. Given the complexity of these reaction processes, it is recommended that the reader consider the application of geochemical reaction codes, and surface complexation models in particular, as the best approach to predicting the role of dissolved carbonate in the adsorption behavior of uranium and derivation of K_d values when site-specific K_d values are not available for U(VI).

J.2.0 Availability of K_d Values for Uranium

More than 20 references were identified that reported the results of K_d measurements for the sorption of uranium onto soils, crushed rock material, and single mineral phases. These studies were typically conducted to support uranium migration investigations and safety assessments associated with the genesis of uranium ore deposits, remediation of uranium mill tailings, agriculture practices, and the near-surface and deep geologic disposal of low-level and high-level radioactive wastes (including spent nuclear fuel).

A large number of laboratory uranium adsorption/desorption and computer modeling studies have been conducted in the application of surface complexation models (see Chapter 5 and Volume I) to the adsorption of uranium to important mineral adsorbates in soils. These studies are also noted below.

Several published compilations of K_d values for uranium and other radionuclides and inorganic elements were also identified during the course of this review. These compilations are also briefly described below for the sake of completeness because the reported values may have applicability to sites of interest to the reader. Some of the K_d values in these compilations are tabulated below, when it was not practical to obtain the original sources references.

J.2.1 Sources of Error and Variability

The K_d values compiled from these sources show a scatter of 3 to 4 orders of magnitude at any pH value from pH 4 to 9. As will be explained below, a significant amount of this variation represents real variability possible for the steady-state adsorption of uranium onto soils resulting from adsorption to important soil mineral phases (*e.g.*, clays, iron oxides, clays, and quartz) as a function of important geochemical parameters (*e.g.*, pH and dissolved carbonate concentrations). However, as with most compilations of K_d values, those in this report and published elsewhere, reported K_d values, and sorption information in general, incorporate diverse sources of errors resulting from different laboratory methods (batch versus column versus *in situ* measurements), soil and mineral types, length of equilibration (experiments conducted from periods of hours to weeks), and the fact that the K_d parameter is a ratio of 2 concentrations. These sources of error are discussed in detail in Volume I of this report.

Taking the ratio of 2 concentrations is particularly important to uranium, which, under certain geochemical conditions, will adsorb to soil at less than 5 percent (very small K_d) or up to more than 95 percent (very large K_d) of its original dissolved concentration. The former circumstance (<5 percent adsorption) requires the investigator to distinguish very small differences in the analyzed initial and final concentrations of dissolved uranium. On the other hand, the latter circumstance (>95 percent adsorption) requires analysis of dissolved uranium concentrations that are near the analytical minimum detection limit. When comparing very small or very large K_d values published in different sources, the reader must remember this source of uncertainty can be the major cause for the variability.

In the following summaries, readers should note that the valence state of uranium is given as that listed in the authors' publications. Typically, the authors describe their procedures and results in terms of "uranium," and do not distinguish between the different valence states of uranium [U(VI) and U(IV)] present. In most studies, it is fair for the reader to assume that the authors are referring to U(VI) because no special precautions are described for conducting the adsorption studies using a dissolved reductant and/or controlled environmental chamber under ultralow oxygen concentrations. However, some measurements of uranium sorption onto crushed rock materials may have been compromised unbeknownst to the investigators by reduction of U(VI) initially present to U(IV) by reaction with ferrous iron [Fe(II)] exposed on fresh mineral surfaces. Because a major decrease of dissolved uranium typically results from this reduction due to precipitation of U(IV) hydrous-oxide solids (*i.e.*, lower solubility), the measured K_d values can be too large as a measure of U(VI) sorption. This scenario is possible when one considers the geochemical processes associated with some *in situ* remediation technologies currently under development. For example, Fruchter *et al.* (1996) [also see related paper by Amonette *et al.* (1994)] describe development of a permeable redox barrier remediation technology that introduces a reductant (sodium dithionite buffered at high pH) into contaminated sediment to reduce Fe(III) present in the sediment minerals to Fe(II). Laboratory experiments have shown that dissolved U(VI) will accumulate, via reduction of U(VI) to U(IV) and subsequent precipitation as a U(IV) solid, when it contacts such treated sediments.

J.2.2 Uranium K_d Studies on Soils and Rock Materials

The following sources of K_d values considered in developing the uranium K_d look-up table are listed in alphabetical order. Due to their extensive length, summary tables that list the uranium K_d values presented or calculated from data given in these sources are located at the end of this appendix.

Ames *et al.* (1982) studied the adsorption of uranium on 3 characterized basalts and associated secondary smectite clay. The experiments were conducted at 23 and 60°C under oxidizing conditions using 2 synthetic groundwater solutions. The compositions of the solutions were based on those of groundwater samples taken at depth from the Columbia River basalt formations. The basalts were crushed, and the 0.85-0.33 mm size fraction used for the adsorption studies. The groundwater solutions were mixed with the basaltic material and smectite in a ratio of 10 ml/1 g, and equilibrated for 60 days prior to analysis. Four initial concentrations of uranium (1.0×10^{-4} , 1.0×10^{-5} , 1.0×10^{-6} , and 1.0×10^{-7} M uranium) were used for the measurements. The pH values in the final solutions ranged from 7.65 to 8.48. Uranium K_d values listed as “D” values in Ames *et al.* (1982, Table III) for the 23°C sorption measurements are listed in Table J.5.

Bell and Bates (1988) completed laboratory uranium (and other radionuclides) K_d measurements designed to evaluate the importance of test parameters such as pH, temperature, groundwater composition, and contact time at site-relevant conditions. Materials used for the K_d measurements included a sample of borehole groundwater that was mixed in a solution-to-solid ratio of 10 ml/1 g with the <5-mm size fraction of each of 5 soil materials. For the experiments conducted as a function of pH, the initial pH of the groundwater samples was adjusted by the addition of HCl, NaOH, or NH_4OH . The soils included a glacial till clay, sand, and 3 coarse granular deposits (listed as C1:2, C.3, and C.6 by Bell and Bates). The K_d values were measured using a batch method where the test vessel was agitated continuously at a fixed temperature for a pre-determined length of time. The uranium K_d values measured for the 5 soils at pH 5.7 and 15°C sampled at 14 days are listed in Table J.5. Bell and Bates noted that steady-state conditions were seldom achieved for 14 days contact at pH 5.7 and 15°C. For the clay and C1:2 soils, which exhibited the low-sorptive properties, the uranium K_d values doubled for each temperature increase of 5°. No significant temperature dependence was observed in the uranium K_d values measured using the other 3 soil materials. The uranium K_d values measured as a function of pH showed a maximum in sorption near pH 6 and 10, for the sand and clay soils. However, these 7-day experiments were affected by kinetic factors.

Erickson (1980) measured the K_d values for several radionuclides, including uranium, on abyssal red clay. The dominant mineral in the clay was iron-rich smectite, with lesser amounts of phillipsite, hydrous iron and manganese oxides. The K_d values were measured using a batch equilibration technique with equilibration times of 2-4 days and an initial concentration of dissolved uranium of approximately 3.1×10^{-8} mg/ml. The uranium K_d values measured at pH values of 2.8 and 7.1 by Erickson (1980) are listed in Table J.5.

Erikson *et al.* (1993) determined the K_d values for the adsorption of uranium on soil samples from the U.S. Department of Army munition performance testing sites at Aberdeen Proving Ground, Maryland, and Yuma Proving Ground, Arizona. The soil samples included 2 silt loams (Spesutie and Transonic) from the Aberdeen Proving Ground, and sandy loam (Yuma) from the Yuma Proving Ground. The names of the soil samples were based on the sampling locations at the study sites. The K_d measurements for the Spesutie and Transonic soil samples were conducted with site-specific surface water samples. Because no representative surface water existed at the Yuma site, the soil was equilibrated with tap water. The soil samples were equilibrated in a ratio of 30 ml/1 g with water samples spiked with 200 $\mu\text{g/l}$ uranium. The water/soil mixtures were sampled at 7 and 30 days. The K_d results are given in Table J.5. The K_d values reported for the 30-day samples are 4360 (pH 6.8), 328 (pH 5.6), and 54 ml/g (pH 8.0), respectively, for the Spesutie, Transonic, and Yuma soils. The lower K_d values measured for the Yuma Soil samples were attributed to carbonate complexation of the dissolved uranium.

Giblin (1980) determined the K_d values for uranium sorption on kaolinite as a function of pH in a synthetic groundwater. The measurements were conducted at 25°C using a synthetic groundwater (Ca-Na-Mg-Cl-SO₄) containing 100 $\mu\text{g/l}$ uranium. Ten milliliters of solution was mixed with 0.01 g of kaolinite for a solution-to-solid ratio of 1,000 ml/1 g. The pH of the suspension was adjusted to cover a range from 3.8 to 10. Uranium K_d values from Giblin (1980, Figure 1) are given in Table J.5.¹ Giblin's results indicate that adsorption of uranium on kaolinite in this water composition was negligible below pH 5. From pH 5 to 7, the uranium K_d values increase to a maximum of approximately 37,000 ml/g. At pH values from 7 to 10, the uranium adsorption decreased.

Kaplan *et al.* (1998) investigated the effects of U(VI) concentration, pH, and ionic strength on the adsorption of U(VI) to a natural sediment containing carbonate minerals. The sediments used for the adsorption measurements were samples of a silty loam and a very coarse sand taken, respectively, from Trenches AE-3 and 94 at DOE's Hanford Site in Richland, Washington. Groundwater collected from an uncontaminated part of the Hanford Site was equilibrated with each sediment in a ratio of 2 ml/1 g for 14 or 30 days. The K_d values listed in Kaplan *et al.* (1998) are given in Table J.5. The adsorption of U(VI) was determined to be constant for concentrations between 3.3 and 100 $\mu\text{g/l}$ UO₂²⁺ at pH 8.3 and an ionic strength of 0.02 M. This result indicates that a linear K_d model could be used to describe the adsorption of U(VI) at these conditions. In those experiments where the pH was greater than 10, precipitation of U(VI)-containing solids occurred, which resulted in apparent K_d values greater than 400 ml/g.

Kaplan *et al.* (1996) measured the K_d values for U(VI) and several other radionuclides at geochemical conditions being considered in a performance assessment for the long-term disposal of radioactive low-level waste in the unsaturated zone at DOE's Hanford Site in Richland,

¹ The uranium K_d values listed in Table J.5 for Giblin (1980) were provided by E. A. Jenne (PNNL, retired) based on work completed for another research project. The K_d values were generated from digitization of the K_d values plotted in Giblin (1980, Figure 1).

Washington. The studies included an evaluation of the effects of pH, ionic strength, moisture content, and radionuclide concentration on radionuclide adsorption behavior. Methods used for the adsorption measurements included saturated batch adsorption experiments, unsaturated batch adsorption experiments, and unsaturated column adsorption experiments based on the Unsaturated Flow Apparatus (UFA). The measurements were conducted using uncontaminated pH 8.46 groundwater and the <2-mm size fraction of sediment samples collected from the Hanford Site. The sediment samples included TBS-1 Touchet Bed sand, Trench AE-3 silty loam, Trench-8 medium coarse sand, and Trench-94 very coarse sand. Dominant minerals identified in the clay-size fraction of these sediment samples included smectite, illite, vermiculite, and plagioclase. The reader should refer to Table 2.3 in Kaplan *et al.* (1996) for a listing of the physical and mineralogical properties of these sediment samples. Uranium K_d values estimated from results plotted in Kaplan *et al.* [1996, Figure 3.1 (400-day contact), Figure 3.2 (all values as function of dissolved uranium concentrations), and Figure 3.5 (100 percent saturation values) are listed in Table J.5. Their results show that U(VI) K_d values increased with increasing contact time with the sediments. For the concentration range from 3.3 to 100 $\mu\text{g/l}$ dissolved uranium, the U(VI) K_d values were constant. The U(VI) K_d values increased from 1.1 to 2.2 ml/g for pH values of 8 and 10, respectively, for these site-specific sediments and geochemical conditions. Kaplan *et al.* noted that, at pH values above approximately 10, the measured K_d values were affected by precipitation of uranium solids. Their measurements also indicated that U(VI) K_d values varied as a function of moisture content, although the trend differed based on sediment type. For a coarse-grained sediment, Kaplan *et al.* noted the K_d values increased with increasing moisture saturation. However, the opposite trend was observed for the U(VI) K_d values for fine-grained sediments. Kaplan *et al.* proposed that this behavior was related to changes in tortuosity and effective porosity within the fine pore spaces.

Kaplan and Serne (1995, Table 6.1) report K_d values for the adsorption of uranium on loamy sand sediment taken from Trench 8 at DOE's Hanford Site in Richland, Washington. The measurements were made using a column technique at unsaturated conditions (7 to 40 percent saturated), neutral-to-high pH, low organic material concentrations, and low ionic strength ($I \leq 0.1$). The aqueous solutions consisted of a sample of uncontaminated groundwater from the Hanford Site. The K_d values listed in Kaplan and Serne (1995) are given in Table J.5. The K_d values ranged from 0.08 to 2.81 ml/g, and typically increase with increasing degree of column saturation. Kaplan and Serne noted that K_d values measured using a batch technique are usually greater than those obtained using the column technique due to the greater residence time and greater mixing of the sediment and aqueous phase associated with the batch method.

Lindenmeier *et al.* (1995) conducted a series of flow-through column tests to evaluate contaminant transport of several radionuclides through sediments under unsaturated (vadose zone) conditions. The sediments were from the Trench 8 (W-5 Burial Ground) from DOE's Hanford Site in Richland, Washington. The <2-mm size fraction of the sediment was used for the measurements. The <2-mm size fraction had a total cation exchange capacity (CEC) of 5.2 meq/100 g, and consisted of 87 percent sand, 7 percent silt, and 6 percent clay-size materials. Mineralogical analysis of <2-mm size fraction indicated that it consisted of 43.0 wt.% quartz,

26.1 wt.% plagioclase feldspar, and minor amounts of other silicate, clay, hydrous oxide, and carbonate minerals. The column tests were run using a site-specific groundwater and standard saturated column systems, commercial and modified Wierenga unsaturated column systems, and the Unsaturated Flow Apparatus (UFA). The results of the column tests indicated that the K_d values for uranium on this sediment material decrease as the sediment becomes less saturated. A K_d value of 2 ml/g was determined from a saturated column test conducted at a pore water velocity of 1.0 cm/h and residence time of 1.24 h. However, at 29 percent water saturation, the measured K_d value decreases by 70 percent to 0.6 ml/g (pore water velocity of 0.3 cm/h and residence time of 20.6 h). The K_d values listed in Lindenmeier *et al.* (1995, Table 4.1) are given in Table J.5.

Salter *et al.* (1981) investigated the effects of temperature, pressure, groundwater composition, and redox conditions on the sorption behavior of several radionuclides, including uranium, on Columbia River basalts. Uranium K_d values were determined at 23 and 60°C under oxidizing and reducing conditions using a batch technique. The measurements were conducted with 2 synthetic groundwater solutions (GR-1 and GR-2) that have compositions representative of the groundwater present in basalt formations at DOE's Hanford Site, Richland, Washington. The GR-1 and GR-2 solutions represent a pH 8 sodium bicarbonate-buffered groundwater and a pH 10 silicic acid-buffered groundwater. The synthetic groundwater solutions were mixed with the crushed basalt material (0.03-0.85 mm size fraction) in a ratio of 10 ml/1 g. The contact time for the measurements was approximately 60 days. The K_d values were determined for initial concentrations of 1.0×10^{-4} , 1.0×10^{-5} , 1.0×10^{-6} , 1.0×10^{-7} , and 2.15×10^{-8} M uranium. The K_d values listed in Table J.5 from Salter *et al.* (1981) include only those for 23°C under oxidizing conditions. The reader is referred to Salter *et al.* (1981) for a description of the measurement procedure and results for reducing conditions.

Serkiz and Johnson (1994) (and related report by Johnson *et al.*, 1994) investigated the partitioning of uranium on soil in contaminated groundwater downgradient of the F and H Area Seepage Basins at DOE's Savannah River Site in South Carolina. Their study included determination of an extensive set of field-derived K_d values for ^{238}U and ^{235}U for 48 soil/porewater samples. The K_d values were determined from analyses of ^{238}U and ^{235}U in soil samples and associated porewaters taken from contaminated zones downgradient of the seepage basins. It should be noted that the mass concentration of ^{235}U is significantly less than (*e.g.*, <1 percent) the concentration of ^{238}U in the same soil sample and associated porewater. Serkiz and Johnson used the geochemical code MINTQA2 to model the aqueous complexation and adsorption of uranium in their analysis of migration and partitioning in the contaminated soils. Soil/porewater samples were collected over a range of geochemical conditions (*e.g.*, pH, conductivity, and contaminant concentration). The field-derived uranium K_d listed for ^{238}U and ^{235}U by Serkiz and Johnson are given in Table J.5. The uranium K_d values varied from 1.2 to 34,000 ml/g over a pH range from approximately 3 to 6.7 (Figure J.1). The reader should note that the field-derived K_d values in Figures J.1, J.2, and J.3 are plotted on a logarithmic scale. At these site-specific conditions, the K_d values indicate that uranium adsorption increases with increasing pH over the pH range from 3 to 5.2. The adsorption of uranium is at a maximum at approximately pH 5.2, and then decreases with increasing pH over the pH range from 5.2 to 6.7.

Serkiz and Johnson found that the field-derived K_d values for ^{238}U and ^{235}U were not well correlated with the weight percent of clay-size particles (Figure J.2) or CEC (Figure J.3) of the soil samples. Based on the field-derived K_d values and geochemical modeling results, Serkiz and Johnson proposed that the uranium was not binding to the clays by a cation exchange reaction, but rather to a mineral surface coating with the variable surface charge varying due to the porewater pH.

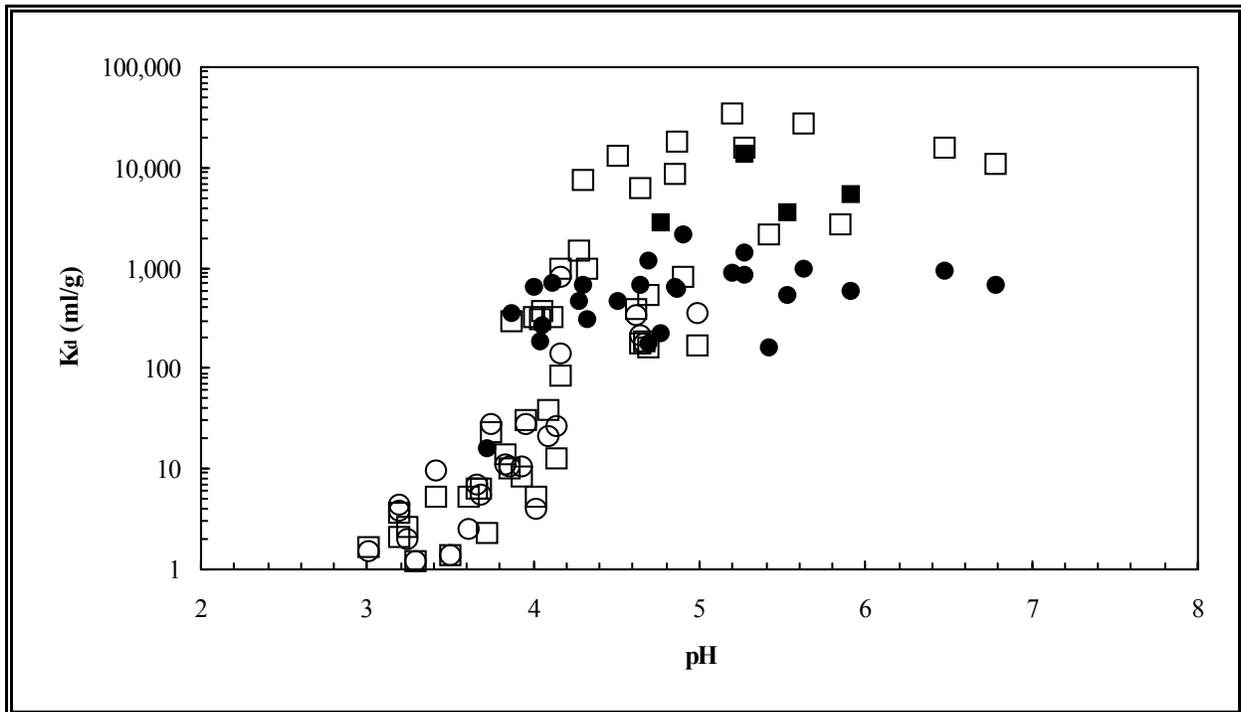


Figure J.1. Field-derived K_d values for ^{238}U and ^{235}U from Serkiz and Johnson (1994) plotted as a function of porewater pH for contaminated soil/porewater samples. [Square and circle symbols represent field-derived K_d values for ^{238}U and ^{235}U , respectively. Solid symbols represent minimum K_d values for ^{238}U and ^{235}U that were based on minimum detection limit values for the concentrations for the respective uranium isotopes in porewaters associated with the soil sample.]

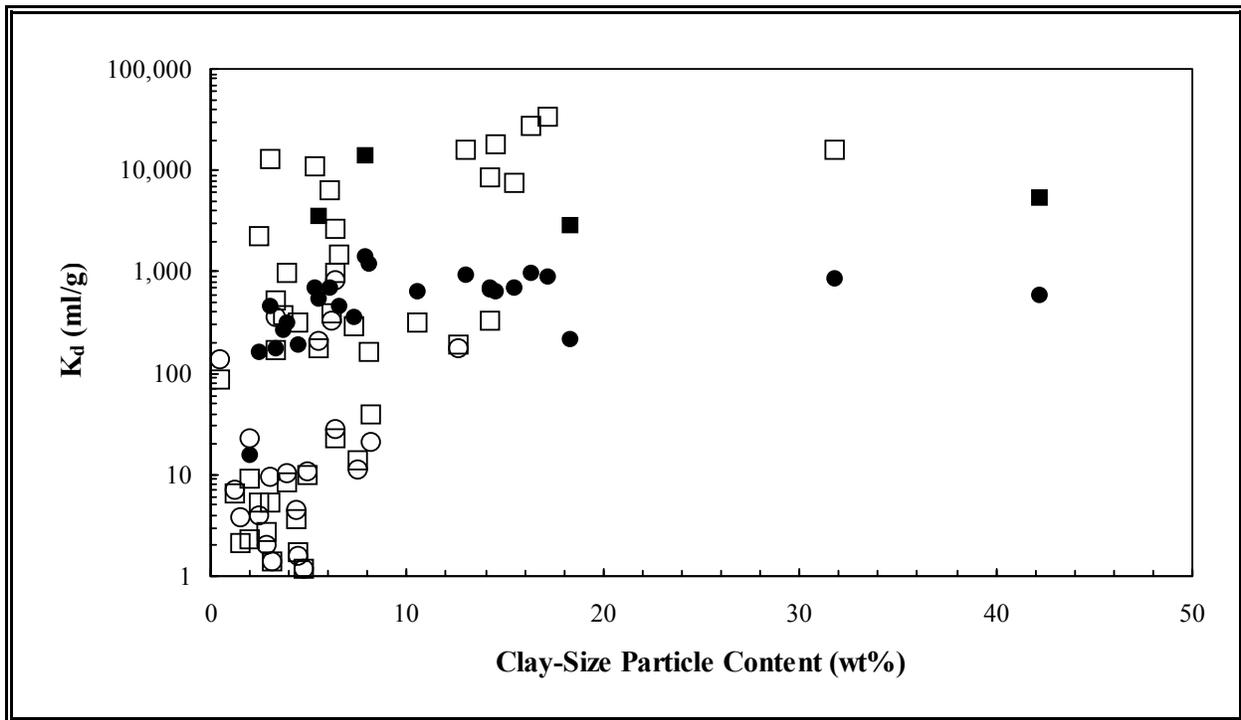


Figure J.2. Field-derived K_d values for ^{238}U and ^{235}U from Serkiz and Johnson (1994) plotted as a function of the weight percent of clay-size particles in the contaminated soil/porewater samples. [Square and circle symbols represent field-derived K_d values for ^{238}U and ^{235}U , respectively. Solid symbols represent minimum K_d values for ^{238}U and ^{235}U that were based on minimum detection limit values for the concentrations for the respective uranium isotopes in porewaters associated with the soil sample.]

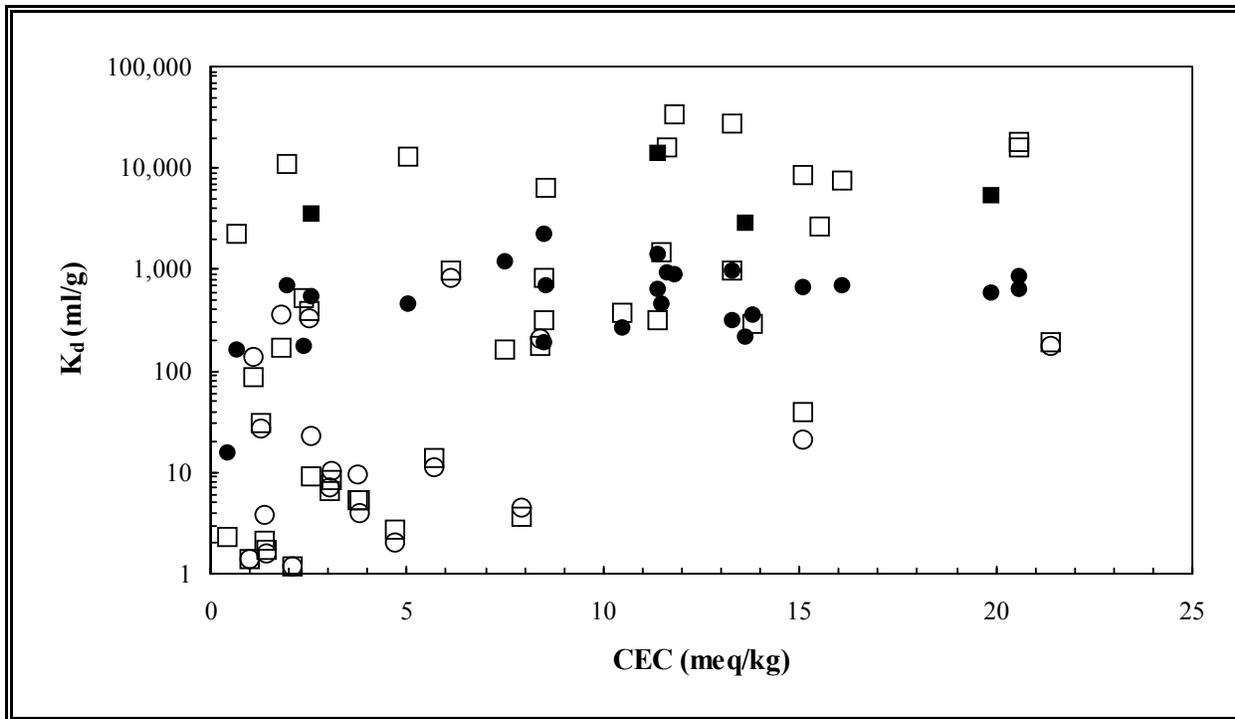


Figure J.3. Field-derived K_d values for ^{238}U and ^{235}U plotted from Serkiz and Johnson (1994) as a function of CEC (meq/kg) of the contaminated soil/porewater samples. [Square and circle symbols represent field-derived K_d values for ^{238}U and ^{235}U , respectively. Solid symbols represent minimum K_d values for ^{238}U and ^{235}U that were based on minimum detection limit values for the concentrations for the respective uranium isotopes in porewaters associated with the soil sample.]

Serne *et al.* (1993) determined K_d values for uranium and several other radionuclides at geochemical conditions associated with sediments at DOE's Hanford Site in Richland, Washington. The K_d values were measured using the batch technique with a well-characterized pH 8.3 groundwater and the <2-mm size fraction of 3 well-characterized sediment samples from the Hanford Site. The sediment samples included TBS-1 Touchet Bed sand, CSG-1 coarse sand/gravel, and Trench-8 medium coarse sand. The <2-mm size fraction of 3 samples consisted of approximately 70 to 90 wt.% plagioclase feldspar and quartz, and minor amounts of other silicate, clay, hydrous oxide, and carbonate minerals. The solution-to-solid ratio was fixed at 30 ml/1 g. The contact time for adsorption measurements with TBS-1, CSG-1, and Trench-8 were, 35, 35, and 44 days, respectively. The average K_d values tabulated for uranium in Serne *et al.* (1993) are given in Table J.5.

Sheppard and Thibault (1988) investigated the migration of several radionuclides, including uranium, through 3 peat¹ types associated with mires² typical of the Precambrian Shield in Canada. Cores of peat were taken from a floating sphagnum mire (samples designated PCE, peat-core experiment) and a reed-sedge mire overlying a clay deposit (samples designated SCE, sedge-core experiment). Uranium K_d values were determined by *in situ* and batch laboratory methods. The *in situ* K_d values were calculated from the ratio of uranium in the dried peat and associated porewater solutions. The batch laboratory measurements were conducted over an equilibration period of 21 days. The in-situ and batch-measured uranium K_d values tabulated in Sheppard and Thibault (1988) are listed in Table J.5. Because the uranium K_d values reported by Sheppard and Thibault (1988) represent uranium partitioning under reducing conditions, which are beyond the scope of our review, these K_d values were not included in Figure J.4. Sheppard and Thibault (1988) noted that the uranium K_d for these 3 peat types varied from 2,00 to 19,000 ml/g, and did not vary as a function of porewater concentration. The laboratory measured K_d values were similar to those determined *in situ* for the SCE peat sample.

Thibault *et al.* (1990) present a compilation of soil K_d values prepared as support to radionuclide migration assessments for a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as uranium, that would be present in the nuclear fuel waste inventory. Some of the uranium K_d values listed by Thibault *et al.* were collected from references that were not available during the course of our review. These sources included studies described in reports by M. I. Sheppard, a coauthor of Thibault *et al.* (1990), and papers by Dahlman *et al.* (1976), Haji-Djafari *et al.* (1981), Neiheisel (1983), Rançon (1973) and Seeley and Kelmers (1984). The uranium K_d values, as listed in Thibault *et al.* (1990), taken for these sources are included in Table J.5.

Warnecke and coworkers (Warnecke *et al.*, 1984, 1986, 1988, 1994; Warnecke and Hild, 1988; and others) published several papers that summarize the results of radionuclide migration experiments and adsorption/desorption measurements (K_d values) that were conducted in support of Germany's investigation of the Gorleben salt dome, Asse II salt mine, and former Konrad iron ore mine as disposal sites for radioactive waste. Experimental techniques included batch and recirculation methods as well as flow-through and diffusion experiments. The experiments were designed to assess the effects of parameters, such as temperature, pH, Eh, radionuclide concentration, complexing agents, humic substances, and liquid volume-to-soil mass ratio, on radionuclide migration and adsorption/desorption. These papers are overviews of the work completed in their program to date, and provide very few details on the experimental designs and individual results. There are no pH values assigned to the K_d values listed in these overview

¹ Peat is defined as “an unconsolidated deposit of semicarbonized plant remains in a water saturated environment” (Bates and Jackson, 1980).

² A mire is defined as “a small piece of marshy, swampy, or boggy ground” (Bates and Jackson, 1980).

papers. Warnecke *et al.* (1984) indicated that the measured pH values for the locations of soil and groundwater samples at Gorleben site studies range from 6 to 9.

Warnecke *et al.* (1994) summarize experiments conducted during the previous 10 years to characterize the potential for radionuclide migration at site-specific conditions at the Gorleben site. Characteristic, minimum, and maximum K_d values tabulated by Warnecke *et al.* (1994, Table 1) for uranium adsorbed to sandy and clayish sediments in contact with fresh or saline waters are listed below in Table J.1. No pH values were assigned to the listed K_d values. Warnecke *et al.* noted that the following progression in uranium K_d values as function of sediment type was indicated:

$$K_d (\text{Clay}) > K_d (\text{Marl}^1) > K_d (\text{Sandy}) .$$

Warnecke and Hild (1988) present an overview of the radionuclide migration experiments and adsorption/desorption measurements that were conducted for the site investigations of the Gorleben salt dome, Asse II salt mine, and Konrad iron ore mine. The uranium K_d values listed in Warnecke and Hild are identical to those presented in Warnecke *et al.* (1994). The uranium K_d values (ml/g) listed by Warnecke and Hild (1988, Table II) for sediments and different water types for the Konrad site are: 4 (Quaternary fresh water), 6 (Turonian fresh water), 6 (Cenomanian saline water), 20 [Albian (Hauterivain) saline water], 1.4 [Albian (Hils) saline water], 2.6 (Kimmeridgian saline water), 3 (Oxfordian saline water), and 3 [Bajocian (Dogger) saline water]. Warnecke and Hild (1988, Table III) list minimum and maximum uranium K_d values (0.54-15.2 ml/g) for 26 rock samples from the Asse II site. No pH values were assigned to any of the tabulated K_d values, and no descriptions were given regarding the mineralogy of the site sediment samples. Warnecke and Hild noted that sorption measurements for the Konrad sediments, especially for the consolidated material, show the same trend as those for the Gorleben sediments.

Table J.1. Uranium K_d values (ml/g) listed by Warnecke *et al.* (1994, Table 1).

Sediment Type	Fresh Water			Saline Water		
	Typical K_d Value	Minimum K_d Value	Maximum K_d Value	Typical K_d Value	Minimum K_d Value	Maximum K_d Value
Sandy	27	0.8	332	1	0.3	1.6
Clayish	17	8.6	100	14 - 1,400	14.1	1,400

¹ Marl is defined as “an earthy substance containing 35-65 percent clay and 65-35 percent carbonate formed under marine or freshwater conditions” (Bates and Jackson, 1980).

Warnecke *et al.* (1986) present an overview of the radionuclide migration experiments and adsorption/desorption measurements that were conducted for the Gorleben salt dome, and Konrad iron ore mine. The tabulated K_d values for the Gorleben and Konrad site sediments and waters duplicate those presented Warnecke *et al.* (1994) and Warnecke and Hild (1988).

Warnecke *et al.* (1984) present a short summary of radionuclide sorption measurements that were conducted by several laboratories in support of the Gorleben site investigation. Sediment (especially sand and silt) and water samples were taken from 20 locations that were considered representative of the potential migration path for radionuclides that might be released from a disposal facility sited at Gorleben. The minimum and maximum K_d values listed by Warnecke *et al.* (1984, Table III) are 0.5 and 3,000 ml/g, respectively (note that these values are not listed as a function of pH).

Zachara *et al.* (1992) studied the adsorption of U(VI) on clay-mineral separates from subsurface soils from 3 DOE sites. The materials included the clay separates (<2 μm fraction) from the Kenoma Formation (Feed Materials Production Center, Fernald, Ohio), Ringold Formation (Hanford Site, Richland, Washington), and Cape Fear Formation (Savannah River Site, Aiken, South Carolina). Prior to the measurements the clay separates were treated with dithionite-citrate buffer and hydrogen peroxide to remove amorphous ferric hydroxides and organic materials. The measurements used clay suspensions (≈ 1 meq of charge/l) spiked with 2 mg/l (8.6 $\mu\text{mol/l}$) uranium and $\text{Ca}(\text{ClO}_4)_2$ or NaClO_4 as the electrolyte. The pH values of the suspensions were adjusted over the pH range from 4.5 to 9.0 using sodium hydroxide. *The measurements were completed in a glovebox under an inert atmosphere to eliminate effects from aqueous complexation of U(VI) by dissolved carbonate.* Uranium K_d values calculated from values of percent uranium adsorbed versus pH (Zachara *et al.*, 1992, Figures 6 and 7) for the Kenoma and Ringold clays are listed in Table J.5.¹ The adsorption results for the Cape Fear clay isolate were essentially the same as those for the Kenoma clay (Zachara *et al.*, 1992, Figures 8). The results for the Kenoma clay isolate show a strong dependence of uranium adsorption as a function of ionic strength that is opposite to that expected for competitive sorption between uranium and the electrolyte cation. Zachara *et al.* (1992) suggest that this increase in uranium adsorption with increasing ionic strength may be due to the ionic strength dependence of the hydrolysis of the uranyl ion.

J.2.3 Uranium K_d Studies on Single Mineral Phases

¹ The uranium K_d values listed in Table J.5 for Zachara *et al.* (1992) were provided by E. A. Jenne (PNNL, retired) based on work completed for another research project. The K_d values were derived from percent uranium adsorbed values generated from digitization of data plotted in Zachara *et al.* (1992, Figures 6 and 7) for the Kenoma and Ringold clay isolates. Due to the inherent uncertainty and resulting exceptionally large K_d values, Jenne did not calculate K_d values from any percent uranium adsorbed values that were greater than 99 percent.

Anderson *et al.* (1982) summarize an extensive study of radionuclides on igneous rocks and related single mineral phases. They report K_d values for U(VI) sorption on apatite, attapulgite (also known as palygorskite), biotite, montmorillonite, and quartz. The K_d values were determined using a batch technique using 10^{-7} - 10^{-9} mol/l uranium concentrations, synthetic groundwater, and crushed (0.045-0.063 mm size fraction) mineral and rock material. The solution-to-solid ratio used in the experiments was 50 ml/1 g. The synthetic groundwater had a composition typical for a Swedish deep plutonic groundwater. Uranium K_d values from Anderson *et al.* (1982, Figure 6a) are given in Table J.5.¹

Ames *et al.* (1983a,b) investigated the effects of uranium concentrations, temperature, and solution compositions on the sorption of uranium on several well-characterized secondary and sheet silicate minerals. The secondary phases studied by Ames *et al.* (1983a, oxide analyses listed in their Table 3) included clinoptilolite, glauconite, illite, kaolinite, montmorillonite, nontronite, opal, and silica gel. The sheet silicate minerals used by Ames *et al.* (1983b, oxide analyses listed in their Table 1) consisted of biotite, muscovite, and phlogopite. The sorption of uranium on each mineral phase was measured with 2 solutions (0.01 M NaCl and 0.01 M NaHCO₃) using 4 initial uranium concentrations. The initial uranium concentrations used for the 25°C experiments included 1.0×10^{-4} , 1.0×10^{-5} , 1.4×10^{-6} , and 4.4×10^{-7} mol/l uranium. The batch experiments were conducted under oxidizing conditions at 5, 25, and 65°C in an environmental chamber. Solutions were equilibrated with the mineral solids in a ratio of 10 ml/1 g. A minimum of 30 days was required for the mineral/solution mixtures to reach steady state conditions. Uranium K_d values calculated from the 25°C sorption results given in Ames *et al.* (1983a, Table 6) are listed in Table J.5.

Ames *et al.* (1983c) studied the effects of uranium concentrations, temperature, and solution compositions on the sorption of uranium on amorphous ferric oxyhydroxide. The sorption of uranium on amorphous ferric oxyhydroxide was measured with 2 solutions (0.01 M NaCl and 0.01 M NaHCO₃) using 4 initial uranium concentrations. The initial uranium concentrations used for the 25°C experiments included 1.01×10^{-4} , 1.05×10^{-5} , 1.05×10^{-6} , and 4.89×10^{-7} mol/l uranium for the 0.01 M NaCl solution, and 1.01×10^{-4} , 1.05×10^{-5} , 1.53×10^{-6} , and 5.46×10^{-7} mol/l uranium for the 0.01 M NaHCO₃ solution. The batch experiments were conducted under oxidizing conditions at 25 and 60°C. The solutions were equilibrated for 7 days with the amorphous ferric oxyhydroxide in a ratio 3.58 l/g of iron in the solid. Uranium K_d values calculated from the 25°C sorption results given in Ames *et al.* (1983c, Table II) are listed in Table J.5. Reflecting the high adsorptive capacity of ferric oxyhydroxide, the K_d values for the 25°C measurements range from approximately 2×10^6 ml/g for the 0.01 M NaCl solution to approximately 3×10^4 ml/g for the 0.01 M NaHCO₃ solution.

¹ The uranium K_d values listed in Table J.5 for Anderson *et al.* (1982) were provided by E. A. Jenne (PNNL, retired) based on work completed for another research project. The K_d values were generated from digitization of the K_d values plotted in Anderson *et al.* (1982, Figure 6a).

Borovec (1981) investigated the adsorption of U(VI) and its hydrolytic complexes at 20°C and pH 6.0 on fine-grained kaolinite, illite, and montmorillonite. The results indicate that the K_d values increase with decreasing concentrations of dissolved uranium. At uranium concentrations less than 10^{-4} mol/l, the uranium K_d values for the individual minerals were constant. The K_d values determined at 20°C and pH 6.0 ranged from 50 to 1,000. The values increased in the sequence K_d (kaolinite) < K_d (illite) < K_d (montmorillonite). Borovec presents the following linear equations for the maximum sorption capacity of uranium (a_m , in meq/100 g) on clays at 20°C and pH 6.0 with respect to CEC (in meq/100 g),

$$a_m = 0.90 \text{ CEC} + 1.56 \quad (r = 0.99522) ,$$

and specific surface (A, in m²/g) of clays,

$$a_m = 0.11 A + 2.05 \quad (r = 0.97232) .$$

J.2.4 Published Compilations Containing K_d Values for Uranium

Baes and Sharp (1983) present a model developed for annual-average, order-of-magnitude leaching constants for solutes in agricultural soils. As part of this model development, they reviewed and determined generic default values for input parameters, such as K_d , in their leaching model. A literature review was completed to evaluate appropriate distributions for K_d values for various solutes, including uranium. Because Baes and Sharp (1983) are cited frequently as a source of K_d values in other published K_d reviews (e.g. Looney *et al.*, 1987; Sheppard and Thibault, 1990), the uranium K_d values listed by Baes and Sharp are reported here for the sake of completeness. Based on the distribution that Baes and Sharp determined for the K_d values for cesium and strontium, they assumed a lognormal distribution for the K_d values for all other elements in their compilation. Baes and Sharp listed an estimated default K_d of 45 ml/g for uranium based on 24 uranium K_d values from 10.5 to 4,400 ml/g for agricultural soils and clays in the pH range from 4.5 to 9.0. Their compiled K_d values represent a diversity of soils, pure clays (other K_d values for pure minerals were excluded), extracting solutions, measurement techniques, and experimental error.

Looney *et al.* (1987) describe the estimation of geochemical parameters needed for environmental assessments of waste sites at DOE's Savannah River Plant in South Carolina. Looney *et al.* list K_d values for several metal and radionuclide contaminants based on values that they found in 1-5 published sources. For uranium, Looney *et al.* list a "recommended" K_d of 39.8 ($10^{1.6}$) ml/g, and a range for its K_d values of 0.1 to 1,000,000 ml/g. Looney *et al.* note that their recommended values are specific to the Savannah River Plant site, and they must be carefully reviewed and evaluated prior to using them in assessments at other sites. Nonetheless, such data are often used as "default values" in radionuclide migration assessment calculations, and are therefore listed here for the sake of completeness. It should be noted that the work of Looney *et al.* (1987) predates the uranium-migration and field-derived uranium K_d study reported for contaminated soils at the Savannah River Site by Serkiz and Johnston (1994) (described above).

McKinley and Scholtis (1993) compare radionuclide K_d sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes. The uranium K_d values listed in McKinley and Scholtis (1993, Tables 1, 2, and 4) are listed in Table J.2. The reader should refer to sources cited in McKinley and Scholtis (1993) for details regarding their source, derivation, and measurement. Radionuclide K_d values listed for cementitious environments in McKinley and Scholtis (1993, Table 3) are not included in Table J.2. The organizations listed in the tables in McKinley and Scholtis (1993) include: AECL (Atomic Energy of Canada Limited); GSF (Gesellschaft für Strahlen- und Umweltforschung m.b.H., Germany); IAEA (International Atomic Energy Agency, Austria); KBS (Swedish Nuclear Safety Board); NAGRA [Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (Swiss National Cooperation for Storage of Radioactive Waste), Switzerland]; NIREX (United Kingdom Nirex Ltd.); NRC (U.S. Nuclear Regulatory Commission); NRPB (National Radiological Protection Board, United Kingdom); PAGIS [Performance Assessment of Geological Isolation Systems, Commission of the European Communities (CEC), Belgium; as well as PAGRIS SAFIR (Safety Assessment and Feasibility Interim Report)]; PSE (Projekt Sicherheitsstudien Entsorgung, Germany); RIVM [Rijksinstituut voor Volksgezondheid en Milieuhygiene (National Institute of Public Health and Environment Protection), Netherlands]; SKI [Statens Kärnkraftinspektion (Swedish Nuclear Power Inspectorate)]; TVO [Teollisuuden Voima Oy (Industrial Power Company), Finland]; and UK DoE (United Kingdom Department of the Environment).

Table J.2. Uranium K_d values listed by McKinley and Scholtis (1993, Tables 1, 2, and 4) from sorption databases used by different international organizations for performance assessments of repositories for radioactive wastes.

Organization	Argillaceous (Clay)		Crystalline Rock		Soil/Soil	
	Sorbing Material	K_d (ml/g)	Sorbing Material	K_d (ml/g)	Sorbing Material	K_d (ml/g)
AECL	Bentonite-Sand	100	Granite	5	Soil/Sediment	20
GSF	Sediment	2				
IAEA	Pelagic Clay	500				
KBS-3	Bentonite	120	Granite	5,000		
NAGRA	Bentonite	1,000	Granite	1,000	Soil/Sediment	20
	Clay	5,000			Soil/Sediment	100
NIREX	Clay Mudstone	10				
NRC	Clay, Soil Shale	20	Granite	5		
			Basalt	4		
			Tuff	300		
NRPB	Clay	300			Soil/Sediment	300
PAGIS	Bentonite	90			Soil/Sediment	1,700
	Subseabed	100				
PAGIS SAFIR	Clay	600				
PSE	Sediment	0.02				
RIVM	Sandy Clay	10				
SKI	Bentonite	200	Granite	5,000		
TVO	Bentonite	90	Crystalline Rock, Reducing	200	Soil/Sediment	500
	Baltic Sea Sediment	500	Crystalline Rock, Real.	5		
	Ocean Sediment	500				
	Lake Sediment	500				
UK DoE	Clay	200			Soil/Sediment	50
	Coastal Marine Water	1000				

In a similar comparison of sorption databases for use in performance assessments of radioactive waste repositories, Stenhouse and Pöttinger (1994) list “realistic” K_d values (ml/g) for uranium

in crystalline rock/water systems of 1,000 (NAGRA), 5,000 [Svensk Kärnbränslehantering AB (Nuclear Fuel and Waste Management Company), Sweden; SKB], 1000 (TVO), and 6 (Canadian Nuclear Fuel Waste Management Programme, CNFWM). For bentonite/groundwater systems, they list 5,000 (NAGRA), 3,000 (SKB), and 500 (TVO). The reader should refer to sources cited in Stenhouse and Pöttinger for details regarding the source, derivation, and measurement of these values.

Thibault *et al.* (1990) [also summarized in Sheppard and Thibault (1990)] updated a compilation of soil K_d values that they published earlier (Sheppard *et al.*, 1984). The compilations were completed to support the assessment(s) of a Canadian geologic repository for spent nuclear fuel in Precambrian Shield plutonic rock. Thibault *et al.* collected K_d values from other compilations, journal articles, and government laboratory reports for important elements, such as uranium, that would be present in the inventory associated with Canada's nuclear fuel wastes. Because Thibault *et al.* (1990) and Sheppard and Thibault (1990) are frequently cited, their derived uranium K_d values are reported here for the sake of completeness. The K_d values for each element were categorized according to 4 soil texture types. These included sand (*i.e.*, contains ≥ 70 percent sand-size particles), clay (*i.e.*, contains ≥ 35 percent clay-size particles), loam (*i.e.*, contains an even distribution of sand-, clay-, and silt-size particles, or ≤ 80 percent silt-size particles), and organic (*i.e.*, contains >30 percent organic matter and are either classic peat or muck sediments, or the litter horizon of a mineral sediment). Based on their previous evaluations, Thibault *et al.* ln-transformed and averaged the compiled K_d values to obtain a single geometric mean K_d value for each element for each soil type. The K_d values for each soil type and the associated range of K_d values listed for uranium by Thibault *et al.* (1990) are given in Table J.3.

Table J.3. Geometric mean uranium K_d values derived by Thibault *et al.* (1990) for sand, loam, clay, and organic soil types.

Soil Type	Geometric Mean K_d Values (ml/g)	Observed Range of K_d Values (ml/g)	Number of K_d Values
Sand	35	0.03 - 2,200	24
Loam	15	0.2 - 4,500	8
Clay	1,600	46 - 395,100	7
Organic	410	33 - 7,350	6

J.3.0 Approach in Developing K_d Look-Up Table

The uranium K_d values listed in Table J.5 are plotted in Figure J.4 as a function of pH. The K_d values exhibit large scatter. This scatter increases from approximately 3 orders of magnitude at pH values below pH 5, to approximately 3 to 4 orders of magnitude from pH 5 to 7, and approximately 4 to 5 orders of magnitude at pH values from pH 7 to 9. This comparison can be somewhat misleading. At the lowest and highest pH regions, it should be noted that 1 to 2 orders of the observed variability actually represent uranium K_d values that are less than 10 ml/g. At pH values less than 3.5 and greater than 8, this variability includes extremely small K_d values of less than 1 ml/g.

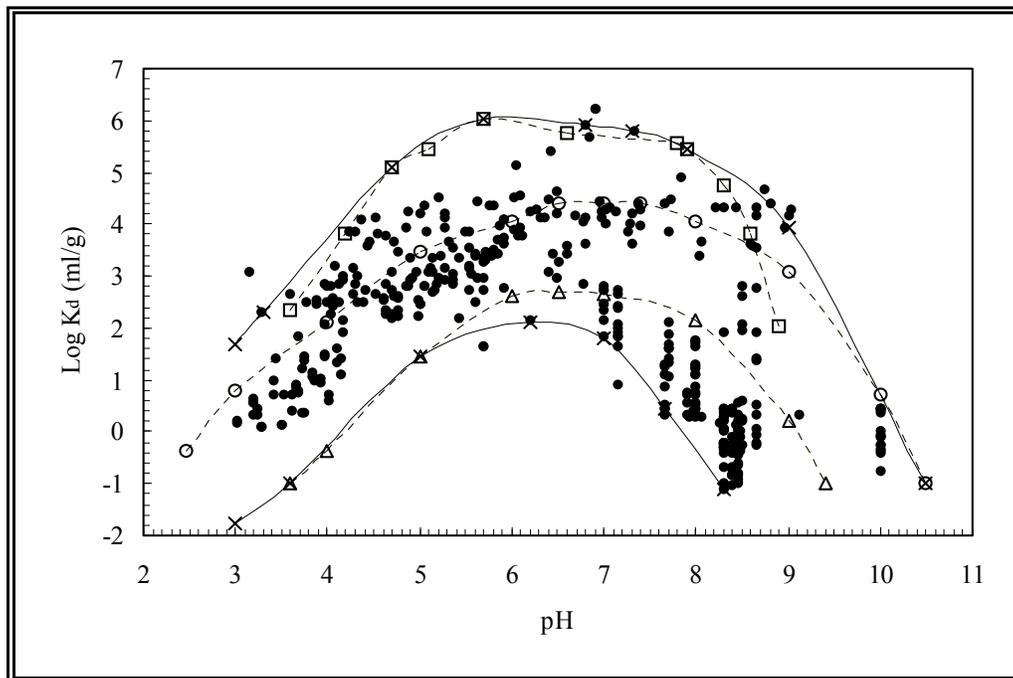


Figure J.4. Uranium K_d values used for development of K_d look-up table. [Filled circles represent K_d values listed in Table J.5. Open symbols (joined by dotted line) represent K_d maximum and minimum values estimated from uranium adsorption measurements plotted by Waite *et al.* (1992) for ferrihydrite (open squares), kaolinite (open circles), and quartz (open triangles). The limits for the estimated maximum and minimum K_d values based on the values in Table J.5 and those estimated from Waite *et al.* (1992) are given by the “x” symbols joined by a solid line.]

J.3.1 K_d Values as a Function of pH

Although the uranium K_d values in Figure J.4 exhibit a great deal of scatter at any fixed pH value, the K_d values show a trend as a function of pH. In general, the adsorption of uranium by soils and single-mineral phases is low at pH values less than 3, increases rapidly with increasing pH from pH 3 to 5, reaches a maximum in adsorption in the pH range from pH 5 to 8, and then decreases with increasing pH at pH values greater than 8. This trend is similar to the *in situ* K_d values reported by Serkiz and Johnson (1994) (see Figure J.1), and percent adsorption values measured for uranium on single mineral phases as described above and those reported for iron oxides (Duff and Amrhein, 1996; Hsi and Langmuir, 1985; Tripathi, 1984; Waite *et al.*, 1992, 1994; and others), clays (McKinley *et al.*, 1995; Turner *et al.*, 1996; Waite *et al.*, 1992; and others), and quartz (Waite *et al.*, 1992). The adsorption data are similar to those of other hydrolyzable metal ions with a sharp pH edge separating low adsorption at low pH from high adsorption at higher pH values. As discussed in the surface complexation laboratory and modeling studies [*e.g.*, Tripathi (1984), Hsi and Langmuir (1985), Waite *et al.* (1992, 1994), and Duff and Amrhein (1996)], this pH-dependent behavior is related to the pH-dependent surface charge properties of the soil minerals and complex aqueous speciation of dissolved U(VI), especially near and above neutral pH conditions where dissolved U(VI) forms strong anionic uranyl-carbonato complexes with dissolved carbonate.

J.3.2 K_d Values as a Function of Mineralogy

In addition to the sources of error and variability discussed above, the scatter in K_d values in Figure J.4 is also related to heterogeneity in the mineralogy of the soils. Soils containing larger percentages of iron oxide minerals and mineral coatings and/or clay minerals will exhibit higher sorption characteristics than soils dominated by quartz and feldspar minerals. This variability in uranium adsorption with respect to mineralogy is readily apparent in uranium K_d values calculated from adsorption measurements (reported as percent uranium adsorbed versus pH) for ferrihydrite, kaolinite, and quartz by Waite *et al.* (1992).

Uranium K_d values were estimated¹ from the plots of percent uranium adsorption given for ferrihydrite, kaolinite, and quartz by Waite *et al.* (1992). To estimate the maximum variability that should be expected for the adsorption of uranium by different mineral substrates, K_d values were calculated from plots of uranium adsorption data for ferrihydrite and kaolinite (minerals with high adsorptive properties) that exhibited the maximum adsorption at any pH from 3 to 10, and for quartz (a mineral with low adsorptive properties) that exhibited the minimum adsorption

¹ The reader is cautioned that significant uncertainty may be associated with K_d values estimated in this fashion because of the extreme solution-to-solid ratios used in some of these studies, especially for highly adsorptive iron-oxide phases, and errors related to estimating the concentrations of sorbed and dissolved uranium based on values for the percent of absorbed uranium near 0 or 100 percent, respectively.

at any pH. These estimated K_d values are shown, respectively, as open squares, circles, and triangles (and joined by dotted lines) in Figure J.4. The difference in the maximum and minimum K_d values is nearly 3 orders of magnitude at any fixed pH value in the pH range from 3 to 9.5. At pH values less than 7, the uranium K_d values for ferrihydrite and quartz calculated from data in Waite *et al.* (1992) bound more than 95 percent of the uranium K_d values gleaned from the literature. Above pH 7, the calculated uranium K_d values for ferrihydrite and kaolinite effectively bound the maximum uranium K_d values reported in the literature.. In terms of bounding the minimum K_d values, the values calculated for quartz are greater than several data sets measured by Kaplan *et al.* (1996, 1998), Lindenmeirer *et al.* (1995), and Serne *et al.* (1993) for sediments from the Hanford Site in Richland, Washington which typically contain a significant quality of quartz and feldspar minerals. It should also be noted that some of the values listed from these studies represent measurements of uranium adsorption on Hanford sediments under partially saturated conditions.

J.3.3 K_d Values As A Function Of Dissolved Carbonate Concentrations

As noted in several studies summarized above and in surface complexation studies of uranium adsorption by Tripathi (1984), Hsi and Langmuir (1985), Waite *et al.* (1992, 1994), McKinley *et al.* (1995), Duff and Amrhein (1996), Turner *et al.* (1996), and others, dissolved carbonate has a significant effect on the aqueous chemistry and solubility of dissolved U(VI) through the formation of strong anionic carbonate complexes. In turn, this complexation affects the adsorption behavior of U(VI) at alkaline pH conditions. Even differences in partial pressures of CO_2 have a major affect on uranium adsorption at neutral pH conditions. Waite *et al.* (1992, Figure 5.7), for example, show that the percent of U(VI) adsorbed onto ferrihydrite decreases from approximately 97 to 38 percent when CO_2 is increased from ambient (0.03 percent) to elevated (1 percent) partial pressures. In those adsorption studies that were conducted in the absence of dissolved carbonate (see surface complexation modeling studies listed above), uranium maintains a maximum adsorption with increasing pH as opposed to decreasing with increasing pH at pH values near and above neutral pH. Although carbonate-free systems are not relevant to natural soil/groundwater systems, they are important to understanding the reaction mechanisms affecting the aqueous and adsorption geochemistry of uranium.

It should be noted that it is fairly common to see figures in the literature or at conferences where uranium adsorption plotted from pH 2 to 8 shows maximum adsorption behavior even at the highest pH values. Such plots may mislead the reader into thinking that uranium adsorption continues this trend (*i.e.*, maximum) to even higher pH conditions that are associated with some groundwater systems and even porewaters derived from leaching of cementitious systems. Based on the uranium adsorption studies discussed above, the adsorption of uranium decreases rapidly, possibly to very low values, at pH values greater than 8 for waters in contact with CO_2 or carbonate minerals .

No attempt was made to statistically fit the K_d values summarized in Table J.5 as a function of dissolved carbonate concentrations. Typically carbonate concentrations were not reported and/or discussed, and one would have to make assumptions about possible equilibrium between the

solutions and atmospheric or soil-related partial pressures of CO₂ or carbonate phases present in the soil samples. As will be discussed in a later section, the best approach to predicting the role of dissolved carbonate in the adsorption behavior of uranium and derivation of K_d values is through the use of surface complexation modeling techniques.

J.3.4 K_d Values as a Function of Clay Content and CEC

No attempt was made to statistically fit the K_d values summarized in Table J.5 as a function of CEC or concentrations of clay-size particles. The extent of clay concentration and CEC data, as noted from information included in Table J.5, is limited to a few studies that cover somewhat limited geochemical conditions. As discussed above, Serkiz and Johnson (1994) found no correlation between their uranium *in situ* K_d values and the clay content (Figure J.2) or CEC (Figure J.3) of their soils. Their systems covered the pH conditions from 3 to 7.

As noted in the studies summarized above, clays have an important role in the adsorption of uranium in soils. Attempts have been made (*e.g.*, Borovec, 1981) to represent this functionality with a mathematical expression, but such studies are typically for limited geochemical conditions. Based on the studies by Chisholm-Brause (1994), Morris *et al.* (1994), McKinley *et al.* (1995), Turner *et al.* (1996), and others, uranium adsorption onto clay minerals is complicated and involves multiple binding sites, including exchange and edge-coordination sites. The reader is referred to these references for a detailed treatment of the uranium adsorption on smectite clays and application of surface complexation modeling techniques for such minerals.

J.3.5 Uranium K_d Look-Up Table

Given the orders of magnitude variability observed for reported uranium K_d values, a subjective approach was used to estimate the minimum and maximum K_d values for uranium as a function of pH. These values are listed in Table J.4. For K_d values at non-integer pH values, especially given the rapid changes in uranium adsorption observed at pH values less than 5 and greater than 8, the reader should assume a linear relationship between each adjacent pair of pH-K_d values listed in Table J.4.

Table J.4. Look-up table for estimated range of K_d values for uranium based on pH.

K _d (ml/g)	pH							
	3	4	5	6	7	8	9	10
Minimum	<1	0.4	25	100	63	0.4	<1	<1
Maximum	32	5,000	160,000	1,000,000	630,000	250,000	7,900	5

The minimum and maximum K_d values listed in Table J.4 were taken from the solid lines plotted in Figure F.4. The area between the 2 solid lines contains more than 95 percent of uranium K_d values collected in this review. The curve representing the minimum limit for uranium K_d values is based on K_d values calculated (described above) for quartz from data given in Waite *et al.* (1992) and the K_d values reported by Kaplan *et al.* (1996, 1998), Lindenmeier *et al.* (1995), and Serne *et al.* (1993). It is unlikely that actual K_d values for U(VI) can be much lower than those represented by this lower curve. At the pH extremes along this curve, the uranium K_d values are already very small. Moreover, if one considers potential sources of error resulting from experimental methods, it is difficult to rationalize uranium K_d values much lower than this lower boundary.

The curve representing the maximum limit for uranium K_d values is based on K_d values calculated (described above) for ferrihydrite and kaolinite from data given in Waite *et al.* (1992). It is estimated that the maximum boundary of uranium K_d values plotted in Figure J.4 is conservatively high, possibly by an order of magnitude or more especially at pH values greater than 5. This estimate is partially based on the distribution of measured K_d values plotted in Figure J.4, and the assumption that some of the very large K_d measurements may have included precipitation of uranium-containing solids due to starting uranium solutions being oversaturated. Moreover, as noted previously, measurements of uranium adsorption onto crushed rock samples may include U(VI)/U(IV) redox/precipitation reactions resulting from contact of dissolved U(VI) with Fe(II) exposed on the fresh mineral surfaces.

J.4.0 Use of Surface Complexation Models to Predict Uranium K_d Values

As discussed in Chapter 4 and in greater detail in Volume I of this report, electrostatic surface complexation models (SCMs) incorporated into chemical reaction codes, such as EPA's MINTEQA2, may be used to predict the adsorption behavior of some radionuclides and other metals and to derive K_d values as a function of key geochemical parameters, such as pH and carbonate concentrations. Typically, the application of surface complexation models is limited by the availability of surface complexation constants for the constituents of interest and competing ions that influence their adsorption behavior.

The current state of knowledge regarding surface complexation constants for uranium adsorption onto important soil minerals, such as iron oxides, and development of a mechanistic understanding of these reactions is probably as advanced as those for any other trace metal. In the absence of site-specific K_d values for the geochemical conditions of interest, the reader is encouraged to apply this technology to predict bounding uranium K_d values and their functionality with respect to important geochemical parameters.

Numerous laboratory surface complexation studies for uranium have been reported in the literature. These include studies of uranium adsorption onto iron oxides (Duff and Amrhein, 1996; Hsi and Langmuir, 1985; Tripathi, 1984; Waite *et al.*, 1992, 1994; and others), clays (McKinley *et al.*, 1995; Turner *et al.*, 1996; Waite *et al.*, 1992; and others), and quartz (Waite *et*

al., 1992; and others). These references include derivation of the surface complexation constants for surface coordination sites determined to be important.

In addition to these laboratory studies, there are numerous examples in the literature of the application of surface complexation models and published binding constants to predict and evaluate the migration of uranium in soil/groundwater systems. For example, Koß (1988) describes the use of a surface complexation adsorption model to calculate the sorption of uranium for soil-groundwater systems associated with the proposed site for a German geologic radioactive waste repository at Gorleben. An apparent constant (*i.e.*, apparent surface complex formation constant based on bulk solution concentrations, K^{app}) was derived for uranium sorption using the MINEQL geochemical code and site-specific geochemical data for soil CEC values, groundwater compositions, and measured uranium K_d values. Quartz (SiO_2) was the main constituent in the soils considered in this study. Because the model incorporates the aqueous speciation of uranium, it may be used to compare K_d values for different soil systems having equal sorption sites. The modeling results indicated that CEC, pH, ionic strength, and dissolved carbonate concentrations were the main geochemical parameters affecting the sorption of uranium in groundwater systems.

Puigdomènech and Bergström (1994) evaluated the use of surface complexation models for calculating radionuclide sorption and K_d values in support of performance assessments studies of geologic repositories for radioactive wastes. They used a triple layer surface complexation model to predict the amount of uranium sorbed to a soil as a function of various environmental parameters. They then derived K_d values based on the concentrations of adsorbed and dissolved uranium predicted by the model. For the surface complexation modeling, they assumed (1) a total uranium concentration of 10^{-5} mol/l, and (2) the adsorption of uranium on soil was controlled by the soil concentration of iron oxyhydroxide solid, which was assumed to be 5 percent goethite [$\alpha\text{-FeO(OH)}$]. Their modeling results indicated that pH, inorganic carbon (*i.e.*, dissolved carbonate), and Eh (redox conditions) are major parameters that affect uranium K_d values. Under oxidizing conditions at pH values greater than 6, their derived K_d values were approximately 100 ml/g. At high concentrations of dissolved carbonate, and pH values greater than 6, the K_d values for uranium decrease considerably. Their results indicate that the triple layer surface complexation model using constants obtained under well controlled laboratory conditions on well characterized minerals can easily be applied to estimate the dependence of uranium adsorption and uranium K_d values as a function of a variety of important site environmental conditions.

Efforts have also been made to compile site binding constants for radionuclides and other metals to create “sorption databases” for use with geochemical codes such as MINTQA2. For example, Turner *et al.* (1993) and Turner (1993, 1995) describe the application of the surface-complexation models (SCMs) [*i.e.*, the diffuse layer model (DLM), constant capacitance model (CCM), and triple layer model (TLM)] in the geochemical reaction code MINTQA2 to simulate potentiometric titration and adsorption data published for U(VI) and other radionuclides on several single mineral phases. Their studies were conducted in support of developing a uniform approach to using surface complexation models to predict radionuclide migration

behavior associated with disposal of high-level radioactive waste in a geologic repository. The parameter optimization code FITEQL was used for fitting and optimization of the adsorption binding constants that were used in conjunction with MINTEQA2 and its thermodynamic database. For those radionuclides having sufficient data, the surface-complexation models were used to examine the effects of changing geochemical conditions (*e.g.*, pH) on radionuclide adsorption. Turner *et al.* (1993) and Turner (1993, 1995) include a detailed listing and documentation of the adsorption reactions and associated binding constants used for the MINTEQA2 DLM, CCM, and TLM calculations. Although all 3 models proved capable of simulating the available adsorption data, the DLM was able to do so using the fewest parameters (Turner, 1995). Compared to empirical approaches (*e.g.*, K_d) for predicting contaminant adsorption, Turner notes that surface complexation models based on geochemical principles have the advantage of being used to extrapolate contaminant adsorption to environmental conditions beyond the range measured experimentally.

J.5.0 Other Studies of Uranium

The following studies and adsorption reviews were identified during the course of this study. Although they typically do not contain uranium K_d data, they discuss aspects of uranium adsorption behavior in soils that might be useful to some readers searching for similar site conditions. These studies and reviews are briefly discussed below.

Ames and Rai (1978) reviewed and evaluated the processes influencing the mobility and retention of radionuclides. Their review for uranium discussed the following published adsorption studies. The following descriptions are paraphrased from in their report.¹

- Dementyev and Syromyatnikov (1968) determined that the maximum adsorption observed for uranium in the pH 6 region is due to the boundary between the dominant uranium aqueous species being cationic and anionic at lower and higher pH values, respectively.
- Goldsztaub and Wey (1955) determined that 7.5 and 2.0 g uranium could be adsorbed per 100 g of calcined montmorillonite and kaolinite, respectively.
- Horr ath (1960) measured an average enrichment factor of 200 to 350 for the adsorption of uranium on peat.
- Kovalevskii (1967) determined that the uranium content of western Siberian noncultivated soils increased as a function of their clay content and that clay soils contained at least 3 times more uranium than sands.

¹ The full citations listed for these references at the end of this appendix are provided exactly as given by Ames and Rai (1978).

- Manskaya *et al.* (1956) studied adsorption of uranium on fulvic acids as a function of pH. Results indicate a maximum removal of uranium of approximately 90 percent at pH 6, and 30 percent removal at pH values of 4 and 7.
- Masuda and Yamamoto (1971) showed that uranium from 1 to 100 mg/l uranium solutions was approximately completely adsorbed by volcanic ash, alluvial, and sandy soils.
- Rancon (1973) investigated the adsorption of uranium on several soils and single minerals. The K_d values reported by Rancon (1973) are (in ml/g): 39 for river sediment (quartz, clay, calcite, and organic matter); 33 for river peat; 16 for soil (quartz, clay, calcite, and no organic matter); 270 for quartz-clay soil developed from an altered schist; 0 for quartz; 7 for calcite; and 139 for illite.
- Ritchie *et al.* (1972) determined that the uranium content of a river sediment increased with decreasing particle size.
- Rozhkova *et al.* (1959) showed a maximum adsorption of uranium on lignite and humic acids between pH 5 and 6.
- Rubtsov (1972) found that approximately 58 percent of the total uranium was associated with the <1- μ m size fraction of forest podzolic mountain soils.
- Starik *et al.* (1958) studied adsorption of uranium on ferric hydroxide as a function of pH. Adsorption was a maximum at pH 5 with 50 percent uranium adsorption and decreased at pH values greater and less than pH 5.
- Szalay (1954, 1957) showed high adsorption of uranium by decomposing plant debris, peat, lignite, and brown coal.
- Yakobenchuck (1968) showed correlations of total uranium content with the silica, iron, and alumina oxide contents in sodpodzolic soils.
- Yamamoto *et al.* (1973) showed that uranium in 1 to 50 mg/l uranium solutions was almost completely adsorbed on 3 solids in carbonate waters.

Brindley and Bastovano (1982) studied the interaction of dissolved U(VI) with commercially available, synthetic zeolites of type A saturated with Na^+ , K^+ , and Ca^{2+} . The experiments consisted of mixing 30 ml of uranyl acetate solution with 50 mg of finely powdered zeolite sample for an equilibration period of 4 days. The initial concentrations and pH values of the uranyl acetate solutions ranged from 100 to 3,700 ppm, and 3.5-3.8, respectively. The reaction of the zeolite with the uranyl acetate solution resulted in pH values in the range from 6 to 8 by exchange of H^+ for exchangeable Na^+ , K^+ , and Ca^{2+} . Examination of the reaction products using X-ray powder diffraction (XRD) indicated the formation of uranium-containing phases

accompanied by unreacted zeolite. The products of the reactions involving Na- and K-A zeolites contained a phase similar to compreignacite ($K_2O \cdot 6UO_3 \cdot 11H_2O$). Those experiments conducted with Ca-A zeolite contained a phase similar to becquerelite ($CaO \cdot 6UO_3 \cdot 11H_2O$).

Ho and coworkers studied the adsorption of U(VI) on a well-characterized, synthetic hematite ($\alpha\text{-Fe}_2\text{O}_3$) sol.¹ Characterization data listed for the hematite sol by Ho and Doern (1985) and cited in other studies by Ho and coworkers included a particle size of 0.12 μm , surface area of 34 m^2/g , isoelectric point² of pH 7.6, and composition of >98 percent $\alpha\text{-Fe}_2\text{O}_3$ and <2 percent $\beta\text{-FeO(OH)}$. Ho and Doern (1985) studied the adsorption of U(VI) on the hematite sol as a function of dissolved U(VI) concentration. Their procedure consisted of mixing 10 ml of the hematite sol (*i.e.*, constant particle concentration of 0.2 g/l) with 10 ml of uranyl nitrate solution. The uranyl solutions and hematite sol were previously prepared at the required concentration, pH, and ionic strength. The mixtures were equilibrated for 16 hr at 25°C. Over the pH range from 3 to 6.2, Ho and Doern determined that adsorption of U(VI) on the hematite sol increased with increasing concentrations of dissolved U(VI). Even though the particles of hematite sol had a net positive charge in the pH range from 3 to 6.2, significant adsorption of U(VI) was measured. The adsorption of U(VI) was greatest at pH of approximately 6.2, and decreased significantly at lower pH values. Ho and Miller (1986) investigated the adsorption of U(VI) from bicarbonate solutions as a function of initial U(VI) concentration over the pH range from 6.5 to 9.1 using the hematite sol described previously. Their experimental procedure was similar to that described by Ho and Doern, except that the measurements were completed using a 1×10^{-3} mol/l NaHCO_3 solution in which its pH was adjusted by the addition of dilute HCl. Over the pH range from 6.5 to 9.1, Ho and Miller determined that the adsorption of uranium decreased abruptly with increasing pH. In experiments conducted with an initial U(VI) concentration of 5×10^{-6} mol/l, the reported percentages of U(VI) adsorbed on the hematite sol were approximately 98, 47, and 26 percent, respectively, at pH values of 7.1, 8.4, and 9.1. Ho and Miller (1985) evaluated the effect of dissolved humic acid on the adsorption of U(VI) by the hematite sol described in Ho and Doern (1985) over the pH range from approximately 4.3 to 6.4. As used by Ho and Miller, the term “humic acid” referred to the “fraction of humic substances soluble in water at $\text{pH} \geq 4.30$.” The results of Ho and Miller (1985) indicate that the adsorption of U(VI) by hematite is affected by the addition of humic acid and that the magnitude of this effect varies with pH and concentration of humic acid. At low humic acid concentration of 3 mg/l, the surface coverage of the hematite by the humic acid is low and the U(VI) adsorption by the hematite sol is similar to that observed for bare hematite particles. However, as the concentration of humic acid increases, the adsorption behavior of U(VI) changes. In the extreme case of a high humic acid concentration of 24 mg/l, the U(VI) adsorption is opposite that observed for bare hematite sol. At intermediate concentrations of humic acid, there is a change

¹ A sol is defined as “a homogeneous suspension or dispersion of colloidal matter in a fluid” (Bates and Jackson, 1980).

² The isoelectric point (iep) is defined as “the pH where the particle is electrokinetically uncharged” (Stumm and Morgan, 1981).

from enhanced U(VI) adsorption at low pH to reduced adsorption at high pH for the pH range from 4.3 to 6.4.

Tsunashima *et al.* (1981) investigated the sorption of U(VI) by Wyoming montmorillonite. The experiments consisted of reacting, at room temperature, the <2- μm size fraction of montmorillonite saturated with Na^+ , K^+ , Mg^{2+} , Ca^{2+} , and Ba^{2+} with U(VI) nitrate solutions containing 1 to 300 ppm U(VI). The tests included systems with fixed volumes and variable uranyl concentrations [50 mg of clay dispersed in 200 ml of U(VI) nitrate solutions with 1-40 ppm U(VI)] and systems with variable volumes and fixed amounts of U(VI) [100 mg clay dispersed in 100 ml of solution]. The duration of the contact period for the clay-solution suspensions was 5 days. Based on the conditions of the constant volume/constant ionic strength experiments, the results indicated that adsorption of uranyl ions (UO_2^{2+}) was strongly preferred over Na^+ and K^+ by the clay, and less strongly preferred versus Mg^{2+} , Ca^{2+} , and Ba^{2+} .

Vochten *et al.* (1990) investigated the adsorption of U(VI) hydrolytic complexes on well-characterized samples of natural zeolites in relation to the double-layer potential of the minerals. The zeolite samples included chabazite ($\text{CaAl}_2\text{Si}_4\text{O}_{12}\cdot 6\text{H}_2\text{O}$), heulandite [$(\text{Ca},\text{Na}_2)\text{Al}_2\text{Si}_7\text{O}_{18}\cdot 6\text{H}_2\text{O}$], scolecite ($\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$), and stilbite [$(\text{Ca},\text{Na}_2,\text{K}_2)\text{Al}_2\text{Si}_7\text{O}_{18}\cdot 7\text{H}_2\text{O}$]. The adsorption measurements were conducted at 25°C over a pH range from 4 to 7.5 using 0.1 g of powdered (35-75 μm) zeolite added to a 50 ml solution of 2×10^{-5} mol/l U(VI). The suspension was shaken for 1 week in a nitrogen atmosphere to avoid the formation of U(VI) carbonate complexes. Given the relatively small dimension of the channels in the zeolite crystal structure and ionic diameter of the non-hydrated UO_2^{2+} ion (3.84 Å), Vochten concluded that the adsorption of U(VI) was on the external surfaces of the zeolites. The results indicate low adsorption of U(VI) to the 4 zeolites from pH 4 to 5. The amount of U(VI) adsorption increases rapidly from pH 5 to 7 with the maximum rate of increase being between pH 6 to 7.¹ The adsorption results indicate that chabazite and scolecite had higher sorptive capacities for U(VI) than heulandite and stilbite.

¹ Based on experimental solubility [e.g., as Krupka *et al.* (1985) and others] and geochemical modeling studies, the authors of this document suspect that Vochten *et al.* (1990) may have exceeded the solubility of U(VI) above pH 5 and precipitated a U(VI) solid, such schoepite ($\text{UO}_3\cdot 2\text{H}_2\text{O}$), during the course of their adsorption measurements conducted in the absence of (or minimal) dissolved carbonate.